

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number  
**WO 2004/055061 A1**

(51) International Patent Classification<sup>7</sup>: C08F 4/64, 4/02

MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number:

PCT/GB2003/005206

(22) International Filing Date: 3 December 2003 (03.12.2003)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

02358031.9 17 December 2002 (17.12.2002) EP

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,  
GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,  
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,

(84) Designated States (regional): ARIPO patent (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,  
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW. ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

**Published:**

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SUPPORTED OFELFIN POLYMERIZATION CATALYST

(57) Abstract: A supported catalyst system comprises (a) a dehydrated support material, (b) a transition metal compound, and (c) an activator and is characterised in that the support material has been pretreated with at least two different organoaluminum compounds prior to contact with either or both the transition metal compound or the activator. The preferred transition metal compound is a metallocene and the supported catalyst systems are suitable for the preparation of polymers having broad molecular weight distributions and improved melt strength.

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## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 9962	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 03/05206	International filing date (day/month/year) 03/12/2003	(Earliest) Priority Date (day/month/year) 17/12/2002
Applicant  BP CHEMICALS LIMITED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
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- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the **title**,

- ☐ the text is approved as submitted by the applicant.
- ☒ the text has been established by this Authority to read as follows:

SUPPORTED OLEFIN POLYMERIZATION CATALYST

5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.
- ☒ None of the figures.

## SUPPORTED CLEFIN POLYMERIZATION CATALYST

### SUPPORTED CATALYSTS

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported catalysts suitable for the preparation of polymers having broad molecular weight distributions and improved melt strengths.

5           In recent years there have been many advances in the production of polyolefin copolymers due to the introduction of transition metal compounds and in particular metallocene catalysts. Metallocene catalysts offer the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature the polyolefin copolymers  
10           produced by metallocene catalysts often are quite uniform in their molecular structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD) and narrow Short Chain Branching Distribution (SCBD). Although certain properties of metallocene products are enhanced by narrow MWD, difficulties are often encountered in the processing of  
15           these materials into useful articles and films relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain structures to be obtained.

          The use of these metal complex based olefin polymerisation catalysts is now well established. Typically the metallocene complex comprises a bis(cyclopentadienyl)  
20           zirconium complex for example bis(cyclopentadienyl) zirconium dichloride or bis(tetramethylcyclopentadienyl) zirconium dichloride. Examples of such complexes may be found in EP 129368, EP 206794, and EP 260130.

          In such catalyst systems the metal complex is used in the presence of a suitable

activator. The activators most suitably used with such metallocene complexes are aluminoxanes, most suitably methyl aluminoxane (MAO). Other suitable activators are boron compounds, in particular perfluorinated boron compounds.

More recently complexes having a single or mono cyclopentadienyl ring have  
5 been developed. Such complexes have been referred to as 'constrained geometry'  
complexes and examples of these complexes may be found in EP 416815 or EP 420436.  
In such complexes the metal atom eg. zirconium or titanium is in the highest oxidation  
state.

Other complexes however have been more recently developed in which the  
10 metal atom may be in a reduced oxidation state. Examples of both the bis  
(cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO  
96/04290 and WO 95/00526 respectively.

The above monocyclopentadienyl metallocene complexes are utilised for  
polymerisation in the presence of a cocatalyst or activator. Typically activators are  
15 aluminoxanes, in particular methyl aluminoxane or compounds based on boron  
compounds. Examples of the latter are boranes, for example tris(pentafluorophenyl)  
borane, or borates such as trialkyl-substituted ammonium tetraphenyl- or  
tetrafluorophenyl-borates. Catalyst systems incorporating such borate activators are  
described in EP 561479, EP 418044 and EP 551277.

20 When used for the gas phase polymerisation of olefins, metallocene complexes  
may typically be supported for example on an inorganic oxide such as silica. Such  
supports may be typically dehydrated by calcining before use or may be pretreated with  
an organoaluminium compound to passivate the surface of the silica.

EP 495849 describes a silica supported catalyst system produced by reacting a  
25 mixture of triisobutylaluminium and trimethylaluminium with the water contained in an  
undehydrated support.

US 5834393 describes in general terms the treatment of support materials with  
organomagnesium, organozinc, organoboron or organoaluminium compounds  
including mixtures thereof. The reference generally describes the use of both  
30 dehydrated and hydrated supports.

WO 91/05810 describes the treatment of undehydrated silica with mixtures of  
trimethylaluminium and triisobutylaluminium to produce silica-aluminoxane products  
subsequently treated with Group IVB and/or Group VB metallocenes.

WO 97/43323 describes in example 7 the addition of triethylaluminium to a calcined silica in the presence of a borate activator. The resultant silica is then further treated with trihexylaluminium.

We have now surprisingly found that when dehydrated supports (ie.  
5 substantially free of water) are pretreated with more than one organoaluminium compound prior to contact with any other catalyst or cocatalyst/activator components the resultant supported catalysts may be used to prepare polymers having broad molecular weight distributions and improved melt strengths.

Thus according to the present invention there is provided a supported catalyst  
10 system comprising

- (a) a dehydrated support material,
- (b) a transition metal compound, and
- (c) an activator

*characterised in that* said support material has been pretreated with at least two  
15 different organoaluminum compounds prior to contact with either or both the transition metal compound or the activator.

By dehydrated support material is meant support material substantially free of water.

Preferred support materials for use in the present invention are particulated solid  
20 support materials.

The support material may be any organic or inorganic inert solid. However particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins, which have well-known advantages in catalysis, are preferred.. Suitable inorganic oxide materials which may be used include Group 2, 13,  
25 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof.

Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed such as finely divided polyolefins such as polyethylene.

30 Suitable volume average particle sizes of the support are from 1 to 1000  $\mu\text{m}$  and preferably from 10 to 100  $\mu\text{m}$ .

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica.

Suitable silicas include Ineos ES70 and Davidson 948 silicas.

The support material may for example be subjected to a heat treatment in order to reduce the water content or the hydroxyl content of the support material. For example prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure, for example, for 5 hrs.

Most preferably the support material is contacted with the organoaluminium compounds at room temperature in a suitable solvent, for example hexane.

Preferred organoaluminium compounds are trialkyl aluminium compounds containing from 1 to 20 carbons atoms in each alkyl group. Preferred trialkylaluminium compounds are trimethylaluminium, triethylaluminium, triisopropylaluminium and triisobutylaluminium.

In the preferred embodiment of the present invention the support material is contacted sequentially with the organoaluminium compounds.

The transition metal compound may be a compound of Groups IIIA to IIB of the Periodic Table of Elements (IUPAC Version). Examples of such transition metal compounds are traditional Ziegler Natta, vanadium and Phillips-type catalysts well known in the art.

The traditional Ziegler Natta catalysts include transition metal compounds from Groups IVA – VIA, in particular catalysts based on titanium compounds of formula  $MR_x$  where M is titanium and R is halogen or a hydrocarbyloxy group and x is the oxidation state of the metal. Such conventional type catalysts include  $TiCl_4$ ,  $TiBr_4$ ,  $Ti(OEt)_3Cl$ ,  $Ti(OEt)_2Br_2$  and similar. Traditional Ziegler Natta catalysts are described in more detail in "Ziegler-Natta Catalysts and Polymerisation" by J.Boor, Academic Press, New York, 1979.

Vanadium based catalysts include vanadyl halides eg.  $VCl_4$ , and alkoxy halides and alkoxides such as  $VOCl_3$ ,  $VOCl_2(OBu)$ ,  $VCl_3(OBu)$  and similar.

Conventional chromium catalyst compounds referred to as Phillips type catalysts include  $CrO_3$ , chromocene, silyl chromate and similar and are described in US 4124532, US 4302565.

Other conventional transition metal compounds are those based on magnesium/titanium electron donor complexes described for example in US 4302565.

Other suitable transition metal compounds are those based on the late transition

metals (LTM) of Group VIII for example compounds containing iron, nickel, manganese, ruthenium, cobalt or palladium metals. Examples of such compounds are described in WO 98/27124 and WO 99/12981 and may be illustrated by [2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>], 2,6-diacetylpyridinebis (2,4,6-trimethylanil) FeCl<sub>2</sub> and [2,6-diacetylpyridinebis(2,6-diisopropylanil)CoCl<sub>2</sub>].

Other transition metal compounds include derivatives of Group IIIA, IVA or Lanthanide metals which are in the +2, +3 or +4 formal oxidation state. Preferred compounds include metal complexes containing from 1 to 3 anionic or neutral ligand groups which may be cyclic or non-cyclic delocalized  $\pi$ -bonded anionic ligand groups.

Examples of such  $\pi$ -bonded anionic ligand groups are conjugated or non-conjugated, cyclic or non-cyclic dienyl groups, allyl groups, boratabenzene groups, phosphole and arene groups. By the term  $\pi$ -bonded is meant that the ligand group is bonded to the metal by a sharing of electrons from a partially delocalised  $\pi$ -bond.

Each atom in the delocalized  $\pi$ -bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl, substituted metalloid radicals wherein the metalloid is selected from Group IVB of the Periodic Table. Included in the term "hydrocarbyl" are C1 – C20 straight, branched and cyclic alkyl radicals, C6 – C20 aromatic radicals, etc. In addition two or more such radicals may together form a fused ring system or they may form a metallocycle with the metal.

Examples of suitable anionic, delocalised  $\pi$ -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, etc. as well as phospholes and boratabenzene groups.

Phospholes are anionic ligands that are phosphorus containing analogues to the cyclopentadienyl groups. They are known in the art and described in WO 98/50392.

The boratabenzenes are anionic ligands that are boron containing analogues to benzene. They are known in the art and are described in Organometallics, 14, 1, 471 – 480 (1995).

The preferred polymerisation catalyst of the present invention is a bulky ligand compound also referred to as a metallocene complex containing at least one of the aforementioned delocalized  $\pi$ -bonded group, in particular cyclopentadienyl ligands. Such metallocene complexes are those based on Group IVA metals for example titanium, zirconium and hafnium.

Metallocene complexes may be represented by the general formula:



5 where L is a cyclopentadienyl ligand, M is a Group IVA metal, Q is a leaving group and x and n are dependent upon the oxidation state of the metal.

Typically the Group IVA metal is titanium, zirconium or hafnium, x is either 1 or 2 and typical leaving groups include halogen or hydrocarbyl. The cyclopentadienyl ligands may be substituted for example by alkyl or alkenyl groups or may comprise a  
10 fused ring system such as indenyl or fluorenyl.

Examples of suitable metallocene complexes are disclosed in EP 129368 and EP 206794. Such complexes may be unbridged eg. bis(cyclopentadienyl) zirconium dichloride, bis(pentamethyl)cyclopentadienyl dichloride, or may be bridged eg. ethylene bis(indenyl) zirconium dichloride or dimethylsilyl(indenyl) zirconium  
15 dichloride.

Other suitable bis(cyclopentadienyl) metallocene complexes are those bis(cyclopentadienyl) diene complexes described in WO 96/04290. Examples of such complexes are bis(cyclopentadienyl) zirconium (2,3-dimethyl-1,3-butadiene) and ethylene bis(indenyl) zirconium 1,4-diphenyl butadiene.

20 Examples of monocyclopentadienyl or substituted monocyclopentadienyl complexes suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277. Suitable complexes may be represented by the general formula:

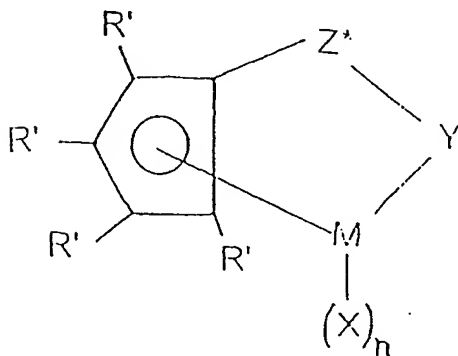


wherein Cp is a single cyclopentadienyl or substituted cyclopentadienyl group optionally covalently bonded to M through a substituent, M is a Group VIA metal bound in a  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl  
30 group, X each occurrence is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms or optionally one X together with Cp forms a metallocycle with M and n is



dependent upon the valency of the metal.

Particularly preferred monocyclopentadienyl complexes have the formula:



5

wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms,

Y is -O-, -S-, -NR<sup>\*</sup>-, -PR<sup>\*</sup>-,

M is hafnium, titanium or zirconium,

Z<sup>\*</sup> is SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>SIR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>CR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup>=CR<sup>\*</sup>, CR<sup>\*</sup><sub>2</sub>SIR<sup>\*</sup><sub>2</sub>, or

20 GeR<sup>\*</sup><sub>2</sub>, wherein:

R<sup>\*</sup> each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R<sup>\*</sup> having up to 10 non-hydrogen atoms, and optionally, two R<sup>\*</sup> groups from Z<sup>\*</sup> (when R<sup>\*</sup> is not hydrogen), or an R<sup>\*</sup> group from Z<sup>\*</sup> and an R<sup>\*</sup> group from Y form a ring system.,

25

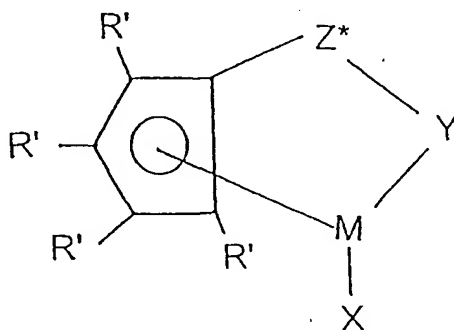
and n is 1 or 2 depending on the valence of M.

Examples of suitable monocyclopentadienyl complexes are (tert-butylamido) dimethyl (tetramethyl- $\eta^5$ -cyclopentadienyl) silanetitanium dichloride and (2-methoxyphenylamido) dimethyl (tetramethyl- $\eta^5$ -cyclopentadienyl) silanetitanium dichloride.

Other suitable monocyclopentadienyl complexes are those comprising phosphinimine ligands described in WO 99/40125, WO 00/05237, WO 00/05238 and WO00/32653. A typical examples of such a complex is cyclopentadienyl titanium [tri (tertiary butyl) phosphinimine] dichloride.

Another type of polymerisation catalyst suitable for use in the present invention are monocyclopentadienyl complexes comprising heteroallyl moieties such as zirconium (cyclopentadienyl) tris (diethylcarbamates) as described in US 5527752 and WO 99/61486.

Particularly preferred metallocene complexes for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the

cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$ -complex with M;

Y is -O-, -S-, -NR<sup>\*</sup>-, -PR<sup>\*</sup>-,

5 M is titanium or zirconium in the + 2 formal oxidation state;

Z<sup>\*</sup> is SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>SIR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>CR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup>=CR<sup>\*</sup>, CR<sup>\*</sup><sub>2</sub>SIR<sup>\*</sup><sub>2</sub>, or

GeR<sup>\*</sup><sub>2</sub>, wherein:

R<sup>\*</sup> each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

10 R<sup>\*</sup> having up to 10 non-hydrogen atoms, and optionally, two R<sup>\*</sup> groups from Z<sup>\*</sup> (when R<sup>\*</sup> is not hydrogen), or an R<sup>\*</sup> group from Z<sup>\*</sup> and an R<sup>\*</sup> group from Y form a ring system.

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; 15 s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, 20 benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire C<sub>5</sub>R'<sub>4</sub> group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C<sub>1-10</sub> 25 hydrocarbyl.

Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the preparation of the supported catalysts of the present invention are those disclosed in WO 95/00526 and are incorporated 30 herein by reference.

A particularly preferred complex for use in the preparation of the supported catalysts of the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -

cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1.3 -pentadiene.

Suitable activators for use with the supports of the present invention include aluminoxanes and organoboron compounds for example boranes.

Aluminoxanes are well known as activators for metallocene complexes.

- 5 Suitable aluminoxanes, for use in the present invention, include polymeric or oligomeric aluminoxanes in particular methyl aluminoxane (MAO).

The aluminoxanes suitable for use in the present invention may be commercially available materials or may be such commercially available material that has been dried under vacuum prior to its use for the preparation of the supported catalyst compositions.

- 10 Preferred organoboron compounds are triarylboron compounds, in particular perfluorinated triarylboron compounds.

The most preferred organoboron compound is tris(pentafluorophenyl) borane (FAB).

- 15 A particularly preferred activator component comprises an organoboron compound and an organoaluminium compound.

The organoaluminium compounds are as described above. The preferred organoaluminium compounds are triethylaluminium or triisobutylaluminium.

Thus according to another aspect of the present invention there is provided a supported catalyst system comprising

- 20 (a) a dehydrated support material,  
(b) a transition metal compound, and  
(c) an activator comprising (i) an organoaluminium compound and (ii) an organoboron compound,

- characterised in that* said support material has been pretreated with at least two  
25 different organoaluminum compounds prior to contact with either or both the transition metal compound or the activator.

For this particular aspect of the present invention the combination of a triarylboron compound for example tris(pentafluorophenyl) borane and a trialkylaluminium compound for example triethylaluminium is preferred as activator.

- 30 The ratio of boron/transition metal in this aspect of the present invention is typically in the range 0.1 to 10 and most preferably in the range 1 to 4.

Other compounds suitable as activators are compounds which comprise a cation and an anion. The cation is typically a Bronsted acid capable of donating a proton and

the anion is typically a compatible non-coordinating bulky species capable of stabilizing the cation.

Such activators may be represented by the formula:



wherein

$L^*$  is a neutral Lewis base

$(L^*-H)^+_d$  is a Bronsted acid

$A^{d-}$  is a non-coordinating compatible anion having a charge of  $d^-$ , and  
 $d$  is an integer from 1 to 3.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic compounds used as activators are those wherein the cation of the ionic compound comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate..

Typical borates suitable as ionic compounds include:

triethylammonium tetraphenylborate  
 triethylammonium tetraphenylborate,  
 tripropylammonium tetraphenylborate,  
 tri(n-butyl)ammonium tetraphenylborate,  
 tri(t-butyl)ammonium tetraphenylborate,  
 N,N-dimethylanilinium tetraphenylborate,  
 N,N-diethylanilinium tetraphenylborate,  
 trimethylammonium tetrakis(pentafluorophenyl) borate,  
 triethylammonium tetrakis(pentafluorophenyl) borate,  
 tripropylammonium tetrakis(pentafluorophenyl) borate,  
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
 N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,

N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

The most preferred activators of this type are those wherein the anion comprises a boron atom.

5 A preferred type of activator suitable for use with the metallocene complexes of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

10 Examples of this type of anion include:

triphenyl(hydroxyphenyl) borate

tri (p-tolyl)(hydroxyphenyl) borate

tris (pentafluorophenyl)(hydroxyphenyl) borate

tris (pentafluorophenyl)(4-hydroxyphenyl) borate

15 Examples of suitable cations for this type of activator include triethylammonium, triisopropylammonium, diethylmethylammonium, dibutylethylammonium and similar.

Particularly suitable are those cations having longer alkyl chains such as dihexyldecylmethylammonium, dioctadecylmethylammonium,  
20 ditetradecylmethylammonium, bis(hydrogenated tallow alkyl) methylammonium and similar.

Particular preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is  
bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-  
25 hydroxyphenyl) borate.

With respect to this type of activator, a preferred compound is the reaction product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an organometallic compound, for example triethylaluminium.

30 The supported catalyst systems of the present invention are most suitable for operation in processes which typically employ supported polymerisation catalysts.

The supported catalysts of the present invention may be suitable for the polymerisation of olefin monomers selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene and (d) mixtures of (a), (b) or (c) with one or more

other alpha-olefins.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of olefin monomers selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene and (d) mixtures of (a), (b) or (c) with  
5 one or more other alpha-olefins, said process performed in the presence of a supported catalyst system as hereinbefore described.

The supported catalyst systems of the present invention are however most suitable for use in slurry or gas phase processes.

A slurry process typically uses an inert hydrocarbon diluent and temperatures  
10 from about 0°C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerisation medium. Suitable diluents include toluene or alkanes such as hexane, propane or isobutane. Preferred temperatures are from about 30°C up to about 200°C but preferably from about 60°C to 100°C. Loop reactors are widely used in slurry polymerisation processes.

15 Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and  $\alpha$ -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art.

Typical operating conditions for the gas phase are from 20°C to 100°C and most preferably from 40°C to 85°C with pressures from subatmospheric to 100 bar.

20 Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the supported catalysts of the present invention.

Particularly preferred polymerisation processes are those comprising the  
25 polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms, said process performed under polymerisation  
30 conditions in the presence of a supported catalyst system as hereinbefore described.

The preferred  $\alpha$ -olefins are 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The supported catalysts prepared according to the present invention may also be suitable for the preparation of other polymers for example polypropylene, polystyrene, etc.

It has been surprisingly found that the supported catalyst systems described herein may be used to prepare copolymers having a broad molecular weight distribution as well as improved melt strengths.

Copolymers may be prepared which exhibit a molecular weight distribution ( $M_w/M_n$ ) of  $> 2$  and preferably  $> 3$ .

The copolymers also exhibit melt strength values (16 Mpa) in the range 3 – 12 cN and preferably in the range 3 – 9 cN.

The copolymers are preferably prepared by use of a supported metallocene catalyst system as hereinbefore described.

Thus according to another aspect of the present invention there is provided a process for the preparation of copolymers of ethylene and alpha-olefins having

- (a) melt strength in the range 3 – 12 cN, and  
(b) a  $M_w/M_n$  of  $> 2$ .

said process comprising contacting ethylene and one or more alpha-olefins in the presence of a supported metallocene catalyst system as hereinbefore described.

The preferred supported catalyst system for this aspect of the present invention is that wherein the transition metal compound is a monocyclopentadienyl metallocene complex as hereinbefore described.

The preferred process for the preparation of such copolymers is a gas phase process.

The present invention also encompasses a dehydrated catalyst support material characterised in that the support material has been treated with at least two different organoaluminium compounds prior to the addition of further catalytic components.

The process of the present invention will now be illustrated by reference to the following examples.

#### Examples

#### Abbreviations used

FAB	tris(pentafluorophenyl)borane
TEA	triethylaluminium
TiBA	trisobutylaluminium



Ionic Activator A  $[N(H)Me(C_{18}H_{37})_2][B(C_6F_5)_3(p-OHC_6H_4)]$   
 Complex A (t-butylamido) (tetramethyl- $\rightarrow^5$ -cyclopentadienyl) dimethyl  
 silanetitanium - $\rightarrow^4$ -1,3-pentadiene

All catalyst preparation steps were performed in a inert atmosphere filled glove-  
 5 box using standard Schlenk and cannulae techniques.

### Example 1

To 5 g of Ineos ES70 silica (previously calcined at 500°C for 5 hours under  
 nitrogen, pore volume 1.55 ml/g) was added 2.04 ml of an hexane solution of  
 triethylaluminium (TEA), 0.98 mol/l, (0.4 mmol Al/ g silica) followed by the addition  
 10 of 1.58 ml of an hexane solution of TiBA, 0.95 mol/l (0.3 mmol Al/g silica). The  
 mixture was allowed to react for 2 hours then dried under vacuum.

To 0.77 g of tris(pentafluorophenyl)borane (1.5 mmol) was added 5 ml of toluene.  
 1.53 ml of a solution of triethylaluminum in hexane, 1 mol/l, were then added and the  
 solution was stirred for 30 minutes.

15 The tris(pentafluorophenyl)borane above was added to the TEA-TiBA treated silica  
 (at pore volume) and then heated at 85°C for 2 hours, followed by drying at the same  
 temperature

1.4 ml of Complex A solution in heptane (9.17 % wt) was then slowly added (15  
 min) and manually agitated until no lumps were visible. After one hour holding the  
 20 catalyst was then dried under vacuum.

$[Ti] = 66 \mu\text{mol/g}$  final catalyst;  $[Al] = 0.908 \text{ mmol/g}$  final catalyst

### Polymerisation data

A 2.5 l double jacketed thermostatic stainless steel autoclave was purged with nitrogen  
 25 at 70°C for at least one hour. PE pellets previously dried under vacuum at 80°C for 12  
 hours were introduced and the reactor was then purged three times with nitrogen (7 bar  
 to atmospheric pressure). ~0.13 g of TEA treated silica (1.5 mmol TEA/g) was added  
 under pressure and allowed to scavenge impurities for at least 15 minutes under  
 agitation. The gas phase was then composed (addition of ethylene, 1-hexene and  
 30 hydrogen) and a mixture of supported catalyst (~0.1 g) and silica/TEA (~0.1 g) was  
 injected. A constant pressure of ethylene and a constant pressure ratio of ethylene/co-  
 monomer were maintained during the run. The run was terminated by venting the

reactor and then purging the reactor 3 times with nitrogen. The PE powder produced during the run was then separated from the PE seed bed by simple sieving.

Typical conditions are as follows:

200 g of PE pellets as bed

5 T = 70°C

PC2= 6.5 Bar.

PC6/PC2 = 0.0048

SiO<sub>2</sub>/TEA impregnated used as scavenger.

H<sub>2</sub> added during the gas phase composition: 150 ml

10 Catalyst quantity: 200 mg

Polymerisation time = 60min

At the end of the polymerisation reaction, polymer produced separated from polymer bed by simple sieving was obtained having the following properties:

	Activity:	24 g/ghb
15	MI (2.16 kg)	0.81 g/10 min
	Density	0.926 g/ml
	Mn	19300 g/mol
	Mw	114125 g/mol
	Mw/Mn	5.9
20	Melt strength(16 Mpa)	7.6 (cN)

### Example 2

To 10 g of Grace 948 silica (previously calcined at 250°C for 5 hours under nitrogen) was added 7.8 ml of an hexane solution of triethylaluminium (TEA), 1.027 mol/l, (0.8 mmol Al/ g silica) followed by the addition of 8.4 ml of an hexane solution of triisobutylaluminium (TiBA), 0.952 mol/l (0.8 mmol Al/g silica). The mixture was  
 25 allowed to react for 2 hours then the silica was decanted, washed three times and dried under vacuum.

[Al] = 1.35 mmol/g (ICP measurment)

30

1.48 mls of a solution of ionic activator A (11.1 wt% in toluene) was reacted with 0.25 ml TEA in toluene (0.25 mol/l) (molar ratio Al/B=0.5). 4g of the above

passivated silica was slowly impregnated (15 min) with the ionic actiator solution and manually agitated until no lumps were visible followed by 30 min holding.

70 ml of Complex A solution in heptane (9.17 % wt) was then slowly added (15 min) and manually agitated until no lumps were visible followed by 30 min holding. 10  
5 ml of hexane was added and the suspension was stirred for 15 minutes. The catalyst was washed 3 times with 20 ml of essence and then dried under vacuum.

$[Ti] = 31 \mu\text{mol/g}$ ;  $[Al] = 1.28 \text{ mmol/g}$

#### 10 Polymerisation data

The same procedure as described above for Example 1 was used.

##### Run conditions

116 g of PE pellets as bed

$T = 70^\circ\text{C}$

15  $PC2 = 6.5 \text{ Bar}$ .

$\% \text{vol C6/PC2} = 0.74$

$\text{SiO}_2/\text{TEA}$  impregnated used as scavenger.

$\text{H}_2$  added during the gas phase composition: 50 ml

catalyst quantity: 103 mg

20 Polymerisation time = 90min

At the end of the polymerisation reaction, polymer produced (77 g) separated from polymer bed by simple sieving

25	Activity:	88 g/ghb
	MI (2.16 kg)	1.02 g/10 min
	MI (21.6 kg)	25.02
	MFR	25
	Density	0.917 g/ml
30	Mn	37000 g/mol
	Mw	114000 g/mol
	Mw/Mn	3.1
	Melt strength (16 Mpa)	3.6 (cN)

Product characteristics were determined using the following analytical procedures:

**Melt Flow Rate (2.16 kg)**

- 5        The melt flow rate (MFR) of the polymers was measured under conditions which conform to ISO 1133 (1991) and BS 2782:PART 720A:1979 procedures. The weight of polymer extruded through a die of 2.095 mm diameter, at a temperature of 190°C, during a 600 second time period and under a standard load of 2.16 kg is recorded.

10      **Molecular Structure Characterisation**

Various techniques (eg  $^{13}\text{C}$  NMR, GPC/LALLS, GPC/intrinsic viscosity, GPC/on-line viscometry and rheological flow activation energy, etc) have been developed to indicate the presence of long chain branching in polymers.

**Molecular Weight Distribution ( $M_w/M_n$ )**

- 15        Molecular weight distribution and associated averages, were determined by Gel Permeation Chromatography using a Waters GPCV 2000. The Millennium version 3.05.01 software supplied by Waters was used for data treatment. The solvent used was 1,2,4 Trichlorobenzene at 150°C, stabilised with 0.05% BHT. The nominal flow rate was 1 ml/min. Solutions of concentration around 0.1%w/w were prepared at 150°C for 20 hours on a hot plate, and the nominal injection volume was set at 217.5 µl. 2 Shodex AT806M/S and 1 Waters HT2 columns were used with a plate count (at half height) of typically 28,000. The system was calibrated using 12 polystyrene standards supplied by Polymer Laboratories.

- 25        Apparent molecular weight distribution and associated averages, uncorrected for long chain branching, were determined using the differential refractometer detector alone. Molecular weight of Ps standards were converted to polyethylene molecular weights using the Mark Houwink parameters  $K_{ps} = 1.75 \times 10^{-4} \text{ dl/g}$ ,  $\alpha_{ps} = 0.67$ ,

$K_{pe} = 4.1 \times 10^{-4} \text{ dl/g}$ ,  $\alpha_{pe} = 0.706$  [Polymer Handbook, J. Bandrup and E.H. Immergut, 3<sup>rd</sup> Edition].

- 30        This calibration has been checked against the NIST certified polyethylene SRM1475, the values obtained being 54,100 g/mol for  $M_w$  and 17,300 g/mol for  $M_n$ .

### Melt Strength

The melt strength of the polymer is measured at 190°C, using a Göttfert Rheotens extensional rheometer in conjunction with a Rosand RH 7 Capillary Rheometer. This is achieved by extruding the polymer at a constant pressure (P) through a die of 1.5 mm diameter and 30 mm in length, with a 90° entry angle. Once a given extrusion pressure is selected, the piston of the capillary rheometer will travel through its 15 mm diameter barrel at a speed that is sufficient to maintain that pressure constant. The nominal wall shear rate ( $\dot{\gamma}$ ) for a given extrusion pressure can then be computed for the polymer at the selected pressure using the constant pressure ratio system of the rheometer.

The extrudate is drawn with a pair of gear wheels at an accelerating speed (V). The acceleration ranges from 0.12 to 1.2 cm/s<sup>2</sup> depending on the flow properties of the polymer under test. The drawing force (F) experienced by the extrudate is measured with a transducer and recorded on a chart recorder together with the drawing speed. The maximum force at break is defined as melt strength (MS) at a constant extrusion pressure (P) or at its corresponding extrusion rate ( $\dot{\gamma}$ ). Three or four extrusion pressures (6, 8, 12, 16 MPa) are typically selected for each polymer depending on its flow properties. For each extrusion pressure, a minimum of 3 MS measurements is performed and an average MS value is then obtained.

The derivative function of the extrusion pressure dependent melt strength,  $\delta(\text{MS})/\delta(\text{P})$  for each polymer is computed from the slope (by a least square line fitting) of the plot of the average MS against pressure. The mean melt strength at an extrusion pressure of 16 MPa, MS (16 MPa), can be computed from the plot.

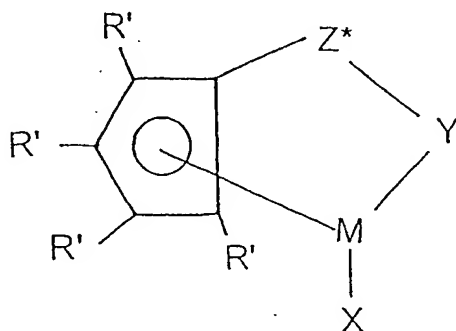
## Claims

1. A supported catalyst composition system comprising
  - (a) a dehydrated support material,
  - (b) a transition metal compound, and
  - (c) an activator
- 5 *characterised in that* said support material has been pretreated with at least two different organoaluminum compounds prior to contact with either or both the transition metal compound or the activator.
2. A supported catalyst system according to claim 1 wherein the support is an particulated solid material.
- 10 3. A supported catalyst system according to claim 2 wherein the support is silica.
4. A supported catalyst system according to any of the preceeding claims wherein the organoaluminium compounds are trialkylaluminium compounds.
5. A supported catalyst system according to any of the preceeding claims wherein the organoaluminium compounds are contacted sequentially with the support material.
- 15 6. A supported catalyst system according to any of the preceeding claims wherein the transition metal compound is a metallocene.
7. A supported catalyst system according to claim 6 wherein the metallocene has the formula:



wherein Cp is a single cyclopentadienyl or substituted cyclopentadienyl group optionally covalently bonded to M through a substituent, M is a Group VIA metal

- bound in a  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group, X each occurrence is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen
- 5 atoms or optionally one X together with Cp forms a metallocycle with M and n is dependent upon the valency of the metal.
8. A supported catalyst system according to claim 6 wherein the metallocene is represented by the general formula:



10 wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the

15 cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$ -complex with M;

Y is -O-, -S-, -NR\*, -PR\*,

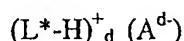
M is titanium or zirconium in the + 2 formal oxidation state;

20 Z\* is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ , wherein:

R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system.

9. A supported catalyst system according to any of the preceeding claims wherein  
5 the activator is an aluminoxane or a borane.
10. A supported catalyst system according to claims 1 to 8 wherein the activator has the formula:



10

wherein

L\* is a neutral Lewis base

$(L^*-H)^+_d$  is a Bronsted acid

$A^{d-}$  is a non-coordinating compatible anion having a charge of  $d^-$ , and

15

d is an integer from 1 to 3.

11. A supported catalyst system according to claim 10 wherein the anion comprises a boron metal.
12. A supported catalyst system according to claim 10 wherein the activator  
comprises a cation and an anion and wherein the anion has at least one substituent  
20 comprising a moiety having an active hydrogen.
13. A supported catalyst system comprising
  - (a) a dehydrated support material,
  - (b) a transition metal compound, and
  - (c) an activator comprising (i) an organoaluminium compound and (ii) an  
25 organoboron compound,

*characterised in that* said support material has been pretreated with at least two different organoaluminum compounds prior to contact with either or both the transition metal compound or the activator.
14. A supported catalyst system according to claim 13 wherein the activator  
30 comprises a trialkylaluminium compound and a triarylboron compound.
15. A process for the polymerisation of olefin monomers selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene and (d) mixtures of (a), (b) or (c) with one or more other alpha-olefins, said process performed under polymerisation



conditions in the presence of a supported catalyst system as claimed in any of the preceding claims.

16. A process for the polymerisation of ethylene or the copolymerisation of ethylene and  $\alpha$ -olefins having from 3 to 10 carbon atoms, said process performed under  
5 polymerisation conditions in the presence of a supported polymerisation catalyst system as claimed in any of claims 1-14.

17. A process according to claims 15 or 16 wherein the  $\alpha$ -olefin is 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene.

18. A process according to any of claims 15 to 17 performed in the solution, slurry  
10 or gas phase.

19. A process according to any of claims 15 to 18 performed in a fluidised bed gas phase reactor.

20. A process for the preparation of copolymers of ethylene and alpha-olefins having

- 15 (a) melt strength (16 Mpa) in the range 3 – 12 cN, and  
(b) a molecular weight distribution ( $M_w/M_n$ ) of  $> 2$ .

said process comprising contacting ethylene and one or more alpha-olefins in the presence of a supported metallocene catalyst system as claimed in any of claims 1 to 14.

21. A dehydrated catalyst support material *characterised in that* said support  
20 material has been pretreated with at least two different organoaluminum compounds prior to the addition of further catalyst components.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 03/05206

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F4/64 C08F4/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 43323 A (DUN JOZEF J VAN ;MIYAMOTO AKIRA (JP); MATSUSHITA FUMIO (JP); CHUM) 20 November 1997 (1997-11-20) example 7	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search

16 March 2004

Date of mailing of the international search report

23/03/2004

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/05206

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9743323	A	20-11-1997	
		JP 9309926 A	02-12-1997
		AT 248866 T	15-09-2003
		AU 3131997 A	05-12-1997
		BR 9710969 A	29-01-2002
		CA 2255754 A1	20-11-1997
		CN 1225101 A ,B	04-08-1999
		CZ 9803728 A3	17-03-1999
		DE 69724607 D1	09-10-2003
		EP 0898586 A1	03-03-1999
		HU 9902561 A2	29-11-1999
		ID 17390 A	24-12-1997
		JP 2001512497 T	21-08-2001
		KR 2000011110 A	25-02-2000
		NO 985329 A	15-01-1999
		NZ 332846 A	26-05-2000
		PL 329949 A1	26-04-1999
		RU 2179558 C2	20-02-2002
		TR 9802352 T2	22-02-1999
		TW 440568 B	16-06-2001
		WO 9743323 A1	20-11-1997
		US 2003055176 A1	20-03-2003
		ZA 9704269 D	16-11-1998